

# A study of the hydrodenitrogenation of propylamine over supported nickel phosphide catalysts using amorphous and nanostructured silica supports

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## Abstract

Pyrolysis of animal by-products provides pyro-oil that contains about 10 wt% nitrogen mainly in aliphatic compounds and virtually no sulfur. The nitrogen should be removed from the oil preferably by hydrodenitrogenation (HDN) to obtain liquid fuel and ammonia. In order to understand the catalytic HDN processes of such bio-oils the HDN of propylamine (PA) was studied as model reaction over silica-supported Ni<sub>2</sub>P and Ni catalysts. Catalysts were prepared by H<sub>2</sub>-reduction of catalyst precursor NiO/phosphated silica gel and NiO/phosphated SBA-15 silica material and NiO/silica gel. The catalyst surface was characterized by Diffuse Reflectance Infrared Fourier Transform Spectroscopic (DRIFTS) examination of adsorbed CO. It was shown that the Ni<sub>2</sub>P particles had a highly defected structure in the initial reduced state of the catalyst but were rapidly converted to ordered crystals in contact with PA under reaction conditions. The HDN reaction of PA was studied using a flow-through tube reactor and also by *in situ* DRIFTS experiments in the 16-60 bar pressure and 200-400 °C temperature range. Below about 300 °C the Ni<sub>2</sub>P catalysts were active in the direct hydrogenolysis of the C-N bond of PA, however, the main reaction was the PA disproportionation to dipropylamine (DPA) and ammonia. Above about 300 °C the hydrogenolysis of the DPA C-N bond became the main reaction. Near to full HDN of PA could be attained without hydrogenolysis of C-C bond. In contrast, Ni/silica gel catalyst was hardly active in the direct C-N hydrogenolysis of PA but was active in the PA disproportionation to DPA. Above about 300 °C reaction temperature ammonia, less propane, and significant amount of methane and ethane were formed.

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## 1. Introduction

Numerous studies have been devoted to the deeper understanding of the catalytic hydrogenation reactions of N-containing organic compounds to support the improvement of hydrodenitrogenation (HDN) technology of petroleum industry [1-3]. The HDN of aromatic molecules was found to begin with full saturation of the N-containing aromatic ring and the formation of primary amine by breaking one C-N bond. The hydrodenitrogenation of nitriles is introduced also by formation of alkylamines. Because mineral oil fractions usually contain also sulfur-compounds the reactions of HDN and hydrodesulfurization (HDS) proceed together. The N-compounds are inhibitors of the HDS reaction, therefore most studies concern the HDN of model compounds over supported or non-supported transition metal sulfides or phosphides in the presence of sulfur compound in the feed. The ammonia was substantiated to be released from quaternized ammonium compound, formed by protonation of the primary amine, on the attack of a nucleophilic  $\text{HS}^-$  or  $\text{S}^{2-}$  species on the catalyst surface [1].

Nowadays more and more attention is focused on the conversion of waste biomass to more favorable energy carrier and energy. Beside the abundantly available lignocellulosic waste materials [4], animal by-products [5], such as meat and bone meal (MBM) represent significant chemical energy and a potential liquid fuel and N-fertilizer resource. Pyrolysis converts a large fraction of the biomass to oily liquid. The pyro-oil gained from animal by-products contains about 10 wt % nitrogen mainly in aliphatic compounds, 5 wt% oxygen and virtually no sulfur [5-7]. By catalytic hydroprocessing of the oil valuable products, preferably hydrocarbons and ammonia are expected to be obtained. The hydrocarbon product can be used as environmental-friendly, carbon dioxide neutral fuel. By converting the ammonia to N-fertilizer, the nitrogen-content of the waste can be recycled to the agriculture. It is a further environmental benefit that the hazardous waste animal by-product is disposed.

The HDN of sulfur-free reaction mixture over nickel phosphide catalyst ( $\text{Ni}_2\text{P}/\text{SiO}_2$ ) was hardly studied before. The present work concerns the HDN of 1-propylamine (PA) over  $\text{Ni}_2\text{P}/\text{SiO}_2$  in a broad pressure and temperature range with the objective to gain better understanding of the reaction mechanism and to provide better scientific bases to the hydroprocessing technology of low sulfur or sulfur-free feeds, rich in organic N-compounds.

## 2. Experimental

### 2.1. Catalyst preparation

Nickel phosphide catalysts supported on silica gel (SYLOBEAD B127, Grace Davison; specific surface area: 563 m<sup>2</sup>/g) or silica material SBA-15 (our synthetic product, synthesized from sodium silicate using a triblock copolymer P123 as template; specific surface area: 800 m<sup>2</sup>/g) were prepared by incipient wetness impregnation followed by calcination and controlled reduction of the nickel phosphide precursor compound according to refs. [2,3]. The impregnating solution was prepared by dissolving 3.04 g (23.0 mmol) of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Fluka, +99%) in 5.0 cm<sup>3</sup> distilled water and adding 3.36 g (11.56 mmol) of Ni(NO<sub>3</sub>)<sub>2</sub> (Merck, +99%) to the solution (initial P/Ni molar ratio of 2). A precipitate was formed. Concentrated cc. HNO<sub>3</sub> solution was added dropwise to the mixture until the precipitate was fully dissolved and a transparent green solution was obtained. This solution was then used to impregnate 10 g of the support previously dried at 120 °C overnight. The impregnated support was dried at 120 °C for 6 h and then calcined at 400 °C for 4 h. Formation of nickel phosphide was effected by treating the samples in 100 cm<sup>3</sup> min<sup>-1</sup> H<sub>2</sub> flow at elevated temperature. The temperature of the samples was raised at a rate of 2 °C min<sup>-1</sup>. The silica gel and the silica SBA-15 supported catalysts were reduced at 650 °C and 700 °C, respectively, for 3-3 hours. The reduction temperatures were chosen based on results of the temperature-programmed reduction (H<sub>2</sub>-TPR) and *in situ* high-temperature X-ray diffraction measurements. Finally, the sample was cooled to room temperature in He flow (20 cm<sup>3</sup> min<sup>-1</sup>) and then contacted with a 50 cm<sup>3</sup> min<sup>-1</sup> flow of 1.0 % O<sub>2</sub>/He for 4 h. Latter treatment aimed to passivate the pyrophoric Ni<sub>2</sub>P particles by generating phosphate-like surface layer that prevents the bulk of the particle to become oxidized when the sample is exposed to air [8-10]. When the obtained material is to be used as catalyst it has to go first through an activating treatment in H<sub>2</sub> flow at 450 °C. The catalyst samples are designated as Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni<sub>2</sub>P/SBA-15. Further on the attribute “passivated” or “activated” or “used” is added to the sample name to refer to the last pretreatment of the preparation that determines the nature of its surface.

For comparative purposes phosphated silica (PO<sub>x</sub>/SiO<sub>2</sub>) and silica supported Ni catalyst were also prepared. The PO<sub>x</sub>/SiO<sub>2</sub> was prepared by impregnating the silica gel support with the same amount of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> than that used for the preparation of Ni<sub>2</sub>P/SiO<sub>2</sub>, however

without adding the Ni precursor to the impregnating solution. The impregnated support was dried at 120 °C for 6 h and then calcined at 450 °C for 4 h. The Ni/SiO<sub>2</sub> catalyst was prepared similarly as silica supported Ni<sub>2</sub>P catalysts, but without adding (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to the impregnating solution. The impregnated support was dried at 120 °C for 6 h and then calcined at 450 °C for 4 h and finally reduced in H<sub>2</sub> flow at 500 °C for 3 h.

## 2.2. Catalyst characterization

### *X-ray powder diffraction (XRD)*

XRD patterns of the samples were obtained with a Philips PW 1810 powder diffractometer, equipped with a graphite monochromator, using Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) and proportional counter. The X-ray tube was set at 40 kV and 35 mA. The step width of scan was 0.04° and, in each step, the counts were digitally recorded. *In situ* X-ray diffraction measurements were carried out using a type HT1200 Anton Paar chamber in order to study the reduction process of the calcined catalyst precursors, i.e. to follow the formation of the active nickel phosphide phase. The samples were heated in H<sub>2</sub> flow from room temperature up to 650 °C at a heating rate of 10 °C min<sup>-1</sup>. The temperature program was stopped at 450, 500, 550, 600, and 650 °C for 30 min. The XRD patterns were recorded after 30 min treatment in H<sub>2</sub> flow at these temperatures. The temperature of H<sub>2</sub> treatment required to get activated catalysts was selected on the bases of these *in situ* high-temperature X-ray diffraction measurements and the H<sub>2</sub>-TPR pattern of the catalyst precursors (see below). XRD patterns of the catalyst samples activated at the selected temperatures were also measured at room temperature. Crystallite sizes were determined from line broadening using the Scherrer equation.

### *Chemical composition*

The nickel and phosphorous content of the as-prepared Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni<sub>2</sub>P/SBA-15 catalysts was determined by ICP-OES analysis.

### *Specific surface area*

The specific surface area of the samples was calculated from isotherms of nitrogen adsorption at 77 K using the BET method. The isotherms were measured by Quantachrome

NOVA Automated Gas Sorption Instrument. The samples were evacuated at 350 °C for 1h before the measurements.

#### *Transmission Electron Microscopy (TEM)*

Diluted suspensions of samples in methanol were prepared and drop-dried on carbon coated copper TEM grids. TEM images were taken by type Morgagni 268D microscope (100 kV, W filament, point-resolution= 0.5 nm).

#### *Temperature-programmed reduction by hydrogen (H<sub>2</sub>-TPR)*

H<sub>2</sub>-TPR was used to determine the reduction temperature required to convert the calcined catalyst precursor to supported nickel phosphide catalyst. The reduction of the catalyst precursors was carried out in a U-shaped quartz tube reactor having an internal diameter of 6 mm. The reactor was placed in a furnace controlled by temperature programmer. The catalyst samples were heated up to 400 °C at a rate of 10 °C min<sup>-1</sup> in nitrogen flow of 30 cm<sup>3</sup> min<sup>-1</sup>, kept at this temperature for 1 h, then cooled to room temperature in nitrogen. The TPR experiment was carried out by changing the N<sub>2</sub> flow to a 30 cm<sup>3</sup> min<sup>-1</sup> flow of 10 % H<sub>2</sub>/N<sub>2</sub>. The effluent gas was passed through a dry-ice trap and a thermal conductivity detector (TCD). Data were collected and processed by computer. According to earlier studies treatment temperatures, higher than that required to generate Ni<sub>2</sub>P phase, was found to result in lowered Ni<sub>2</sub>P dispersion and, as a consequence, in lower hydroconversion activity [11,12]. The TPR results were used to determine the preferable lowest temperature of precursor-to-catalyst conversion and also the H<sub>2</sub> demand of the process.

#### *Temperature-programmed H<sub>2</sub> desorption (H<sub>2</sub>-TPD)*

The H<sub>2</sub>-TPD measurements were carried out on the same instrument that was used for H<sub>2</sub>-TPR measurements. The passivated catalysts were activated in flowing H<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup>) in the reactor tube for 1 h. The pretreatment temperature was 550 °C for Ni<sub>2</sub>P samples and 450 °C for Ni/SiO<sub>2</sub> sample. After reduction the sample was allowed to cool to room temperature in H<sub>2</sub>. The TPD experiment was carried out by changing the H<sub>2</sub> flow to a 30 cm<sup>3</sup> min<sup>-1</sup> flow of N<sub>2</sub>. The catalyst samples were heated up to 600 °C at a rate of 10 °C min<sup>-1</sup> in the N<sub>2</sub> flow and kept at this temperature for 1 h. The reactor effluent was passed through a dry-ice trap and a thermal conductivity detector (TCD). The amount of desorbed H<sub>2</sub> was calculated from the integrated area of the TPD curve. The Ni dispersion in the Ni/SiO<sub>2</sub> catalyst was

calculated according to Subramani et al. [13] as the molar ratio of the Ni on the surface of the particles to the total Ni content. The same method was applied to estimate the dispersion of the supported Ni<sub>2</sub>P phase. The amount of surface Ni atoms was considered as equivalent with the amount of H-atoms in the desorbed H<sub>2</sub> gas.

#### *DRIFTS examination of CO chemisorption*

Carbonyl species obtained from the adsorption of CO on the catalyst was studied by DRIFT spectroscopy using a Nicolet 5PC spectrometer equipped with a COLLECTOR<sup>TM</sup> diffuse reflectance mirror system and a flow-through DRIFT spectroscopic reactor cell (Spectra-Tech, Inc.). The sample cup of the cell was filled with about 20 mg of powdered catalyst sample. The catalyst was reduced first in H<sub>2</sub> flow at 550 °C for 1 h then was purged with He at 550 °C for 1 h, cooled to room temperature and the spectrum of the activated catalyst powder was taken. This spectrum was subtracted from the spectra collected after contacting the sample with a flow of 3% CO/He at room temperature to get characteristic difference spectra. Note that these latter spectra were corrected with the spectrum of gas phase CO in order to remove its contribution from the spectra and thus obtain the spectra of adsorbed CO only. Spectra were taken also after purging the cell with He at room temperature and at 100, 200 and 300 °C for 10 min at each temperature.

### 2.3. Catalytic activity

The 0.315 - 0.63 mm sieve fraction of catalyst particles was filled in a flow-through stainless steel tube microreactor to study the catalytic hydroconversion of PA (Alfa Aesar, 99+%). The PA was fed into the reactor by a high-pressure liquid pump. The hydrogen flow rate and pressure were controlled by electronic mass flow controller (Brooks Instrument Ltd., Hungary) and a back pressure regulator, respectively. The reactor effluent line together with the back pressure regulator and sampling valve were kept at 150 °C in order to avoid condensation in the system. Catalysts were activated in a 100 cm<sup>3</sup> min<sup>-1</sup> hydrogen flow at 450 °C for 1h. The reaction temperature was varied in the range of 200-400 °C at 30 bar total pressure, and at a H<sub>2</sub>/PA molar ratio of 10. The weight hourly space velocity (WHSV) of the reactant PA was varied between 0.75 – 3.0 h<sup>-1</sup>. When the effect of hydrogen partial pressure was studied the H<sub>2</sub>/PA molar ratio and the total pressure was changed between 5 – 20 and 16.2 – 56.7 bar, respectively. Each catalyst samples were tested for about two weeks, while

several measurements at a given set of parameters were repeated in order to check the stability of the catalysts. All the catalysts showed stable activity during this time period. No coke deposition was perceptible to the eye on the catalysts removed from the reactor. The carbon content of the feed and the products was virtually equal. The composition of the reactor effluent was analyzed using on-line a Shimadzu GC-2010Plus type gas chromatograph, equipped with a flame ionization detector and a Supelco EQUITY-1 type capillary column. The main products of the reaction were ammonia, dipropylamine (DPA) and tripropylamine (TPA), propane and, in some experiments, some other lower alkanes. The PA conversion and the NH<sub>3</sub> yield were calculated as follows:

$$\text{Conversion, \%} = ([\text{Propane}] + 2[\text{DPA}] + 3[\text{TPA}]) / ([\text{PA}] + [\text{Propane}] + 2[\text{DPA}] + 3[\text{TPA}]) \times 100,$$

$$\text{Yield of NH}_3, \% = [\text{Propane}] + [\text{DPA}] + 2[\text{TPA}],$$

where the symbols in brackets stand for the molar concentration of the corresponding compounds. The correctness of the calculated ammonia yield was checked by measuring the NH<sub>3</sub> concentration in the reactor effluent. The calculated and the measured data showed only scarce deviation, therefore, the NH<sub>3</sub> yield was routinely determined by calculation.

#### 2.4. DRIFT spectroscopic examination of the HDN reaction

The spectral analysis of the catalyst surface during catalytic HDN of PA was studied using the same DRIFTS apparatus as the one used for the above described CO chemisorption studies. First the catalyst was treated *in situ* in the DRIFTS reactor cell in a 30 cm<sup>3</sup> min<sup>-1</sup> flow of H<sub>2</sub> at 550 °C for 1 h in order to remove the passivating phosphate surface layer of the nickel phosphide particles. On each temperature whereon we run *in situ* catalytic tests in the DRIFTS cell the spectrum of the catalyst powder was recorded in H<sub>2</sub> flow. The reaction was initiated by switching the H<sub>2</sub> flow to a gas saturator containing PA at 0 °C and thus setting 0.14 bar partial pressure of amine in the reaction mixture. The total pressure in the reactor cell was raised from atmospheric to 20 bar using a back pressure regulator upstream the cell. Spectra were then taken at temperatures between 100 and 400 °C. The spectrum obtained from the catalyst and the reacting gas was corrected with the spectrum of the catalyst in H<sub>2</sub> at the reaction temperature. The result is a difference spectrum showing the bands of surface

species and the absorption bands coming from the vibration-rotation modes of molecules in the gas above the operating catalyst.

### 3. Results

#### *XRD and H<sub>2</sub>-TPR results*

The H<sub>2</sub>-TPR curves of the catalyst precursors and the powder XRD patterns of the catalysts obtained by reducing the precursors are given in Fig. 1. The temperature of H<sub>2</sub> treatment required to get activated catalyst, was selected on the bases of the H<sub>2</sub>-TPR pattern of the catalyst precursors and results of *in situ* high-temperature X-ray diffraction measurements (not shown). It was clearly shown that the Ni<sub>2</sub>P phase appears at treatment temperature, whereon H<sub>2</sub> consumption indicates reduction of the precursor compounds on the surface of the silica support. The selected reduction temperature was 500 °C to get Ni/SiO<sub>2</sub>, whereas 650 and 700 °C to obtain Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni<sub>2</sub>P/SBA-15 catalysts, respectively (Fig. 1). The diffraction patterns of the catalysts (Fig. 1B) show diffraction lines located at 2 $\Theta$  degrees of 40.7°, 44.5°, 47.3° and 54.2°, identifying Ni<sub>2</sub>P phase (ICDD card No.: 03-0953). The diffraction lines of the Ni<sub>2</sub>P phase on the higher surface area SBA-15 support are broader, than the corresponding lines of this phase on silica. The reflections of Ni/SiO<sub>2</sub> (Fig. 1B) at 2 $\Theta$  degrees of 44.5° and 51.8° is ascribed to the presence of Ni<sup>0</sup> (ICDD card No.: 04-0852). The broad reflection at about 2 $\Theta$  degrees 15-30° is coming from the amorphous silica support.

The average size of the supported particles, given in Table 1, was calculated by the Scherrer equation using the main diffraction lines of the Ni<sub>2</sub>P and Ni phases at 40.7° and 44.5°, respectively. Data suggest that the mesoporous silica SBA-15 support favors more the formation of highly dispersed Ni<sub>2</sub>P than the microporous silica gel support. The XRD results and the TEM pictures show that the Ni<sup>0</sup> particles in the Ni/SiO<sub>2</sub> catalyst are the smallest (Table 1, Fig. S1). The XRD pattern of the Ni<sub>2</sub>P/SBA-15 catalyst, used in the catalytic PA HDN reaction (not shown), was similar to that of the fresh catalyst, demonstrating that the Ni<sub>2</sub>P morphology was stable under hydrotreating conditions. In contrast, the used Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst present more intense diffraction peaks, suggesting that the Ni<sub>2</sub>P assembled is more ordered crystalline phase than it was in the activated fresh catalyst (Table 1).

It is known that nickel metal easily forms tetracarbonyl and subcarbonyls. Therefore, the determination of Ni dispersion from the CO chemisorption uptake of the Ni catalysts is not suggested. The nickel dispersion (Table 1) was calculated, therefore, from the amount of



chemisorbed  $\text{H}_2$ , determined by  $\text{H}_2$ -TPD (Fig. S2). The average  $\text{Ni}^0$  particle size corresponding to the obtained dispersion was 10.8 nm that was in good agreement with the average particle size obtained from the XRD result and the size of the  $\text{Ni}^0$  particles observed on the TEM pictures. Earlier studies [14-16] used the CO chemisorptions method to determine the  $\text{Ni}_2\text{P}$  dispersion of supported nickel phosphide catalysts. In the present study we attempted to use the  $\text{H}_2$  chemisorption method to estimate the  $\text{Ni}_2\text{P}$  dispersion of our catalysts. Interestingly, much higher dispersions were obtained than for the  $\text{Ni}^0$ . These high dispersions are in obvious contradiction with the average  $\text{Ni}_2\text{P}$  particle size, obtained from the XRD result and observed on the TEM pictures, which are much larger than that of the  $\text{Ni}^0$  particles in the  $\text{Ni}/\text{SiO}_2$  catalyst (Table 1, Fig. 2 and Fig. S1). The contradictory results may indicate that the amount of desorbed H-atoms exceeds the number of surface Ni atoms. It is well known that not only metal atoms can release hydrogen but also surface hydroxyl groups, participating in redox reaction with the supported metal [17] or other surface species. These results suggest that not only the CO but also the  $\text{H}_2$  chemisorption method must be used with extreme caution for the determination of active phase dispersion over oxide support.

#### *DRIFT spectra of the samples and of adsorbed CO*

Fig. 3A shows that the OH-bands of the used catalysts are significantly weaker than those of the activated ones suggesting that adsorbed species consumed OH groups or perturbed  $\nu(\text{OH})$  vibration. To shed light on the nature of the adsorbed species difference spectra were generated by subtracting the spectrum of the activated catalyst from that of the corresponding used one (Fig. 3B). The relatively broad positive bands at  $\sim 3185$ ,  $3030$ , and  $2820\text{ cm}^{-1}$  are due to  $\nu_{\text{NH}}$  vibrations. These bands closely remind of those obtained from adsorption of ammonia on H-zeolites [18] or on Brønsted acid P-OH sites of phosphated silica [19,20]. The bands are assigned to species formed by protonation of ammonia, product of the HDN reaction, or to protonated alkyl amines. The negative  $\nu(\text{OH(P)})$  band at  $3665\text{ cm}^{-1}$  clearly shows the involvement of the P-OH sites in the interaction with the N-bases. The adsorption affects also other P-OH vibrations, for instance the first overtone of the  $\nu_s(\text{P-O(H)})$  vibration that results in the appearance of a negative band at  $2475\text{ cm}^{-1}$  [19]. The band at  $3742$  and the broad band at  $\sim 3515\text{ cm}^{-1}$  stem from vibration of free (terminal) Si-OH groups, and from Si-OH groups, H-bonding to each other, respectively (Fig. 3A). The corresponding negative bands in Fig. 3B suggest that silanol groups were also affected, although silanol hydroxyls cannot protonate ammonia. Therefore, the silanols were either lost by dehydroxylation or the  $\nu(\text{OH})$  frequency

was shifted by H-bonding interaction with adsorbed species. The absorption bands in the range of 2970 – 2870  $\text{cm}^{-1}$  are assigned to  $\nu(\text{CH})$  vibrations of alkyl groups of strongly adsorbed species. Note that not the surface of the active  $\text{Ni}_2\text{P}$  phase was covered by these species since the strength of the carbonyl bands of the activated and the used catalysts was roughly the same (Fig. 4A,B and C,D).

The spectrum of the phosphated silica ( $\text{PO}_x/\text{SiO}_2$ ) sample, treated in He flow at 450 °C, presents sharp bands at 3742 and 3665  $\text{cm}^{-1}$  (Fig. 5, a), which were assigned to  $\nu(\text{OH})$  vibrations of free Si-OH and P-OH groups, respectively [19]. The P-OH groups belong to hydrogen phosphate species, bound to silica by ester bonds, like  $(\text{SiO})_2\text{P}=\text{O}(\text{OH})$ . In the spectrum of the  $\text{Ni}_2\text{P}/\text{SiO}_2$  preparations  $\nu(\text{OH})$  bands appeared at about the same frequencies (Fig. 5, b,c). Before the spectrum of the passivated  $\text{Ni}_2\text{P}/\text{SiO}_2$  (Fig. 5, b) was recorded it was treated at 550°C in He flow. The DRIFT spectrum of the catalyst  $\text{H}_2$ -activated at the same temperature is given in Fig. 5, c. The difference in the pre-treatment temperature of the  $\text{Ni}_2\text{P}/\text{SiO}_2$  and the  $\text{PO}_x/\text{SiO}_2$  preparations explains the found difference in the OH band intensities of the samples. Interestingly, the passivated and the activated catalysts show P-OH band of about the same strength. This result suggests that the amount of P-OH groups over the passivated  $\text{Ni}_2\text{P}$  particles, if any, is negligible relative to the total P-OH concentration of the catalyst sample. The high P-OH concentration is a consequence of the application of phosphate in large stoichiometric excess to nickel in the process of  $\text{Ni}_2\text{P}$  generation [21].

Fig. 4A and 4B shows the DRIFT spectra of the carbonyl species obtained from adsorption of CO on the surface of passivated  $\text{Ni}_2\text{P}/\text{SiO}_2$  (Fig. 4A, a1) and activated ( $\text{H}_2$ -reduced)  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalysts (Fig. 4A, a-e), and on the surface of the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst used prior to the spectroscopic examination in the catalytic HDN reaction of PA (Fig. 4B, a-e). Similar characterization is shown for activated and used  $\text{Ni}_2\text{P}/\text{SBA-15}$  in Fig. 4C and D, respectively.

In the spectra obtained for the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst, being in contact with a flow of atmospheric 3 % CO/He gas, carbonyl band appeared at 2195  $\text{cm}^{-1}$  (Fig. 4A, a1,a). In the spectrum of the passivated catalyst (Fig. 4A, a1) this was the only band, whereas bands of other carbonyls also appeared in that of the pre-reduced catalyst (Fig. 4A, a). Flushing the cell by He flow eliminated the 2195  $\text{cm}^{-1}$  band, suggesting that it came from CO weakly bound to the surface via electrostatic interaction and/or weak  $\sigma$  bond [22,23].

Adsorption of CO on the  $\text{Ni}/\text{SiO}_2$  reference catalyst gave characteristic bands (not shown) at 2070  $\text{cm}^{-1}$  with a shoulder around 2030  $\text{cm}^{-1}$ , and a band at 1925  $\text{cm}^{-1}$  assigned to

the  $\nu(\text{CO})$  vibration of carbonyl groups linearly bound to one Ni atom and adsorbed bridging between two neighboring surface Ni atoms, respectively. From adsorption of CO over activated  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst carbonyl bands were obtained at 2096,  $\sim 2055$  and  $2035\text{ cm}^{-1}$  (Fig. 4A, a). These bands are assigned to carbonyls linearly bound to  $\text{Ni}_2\text{P}$  [21,22,24]. The carbonyls over the  $\text{Ni}_2\text{P}/\text{SiO}_2$  are similar to those, which were found over silica supported Ni catalysts [23,25] but appear at somewhat higher wavenumbers. No carbonyl band was detected below about  $2000\text{ cm}^{-1}$  that would indicate formation of bridging carbonyl groups.

Based on the work of Morandi et al. [26] the bands at 2096 and  $2035\text{ cm}^{-1}$  are assigned here to CO adsorbed on terrace atoms of crystal faces and on high-energy defect sites, respectively. Interestingly, the band at  $2090\text{ cm}^{-1}$  becomes the dominating carbonyl band of the used  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst (Fig. 4B, a-e) suggesting that the  $\text{Ni}_2\text{P}$  phase was re-structured under reaction conditions and took on a less defected structure. The TEM pictures of the fresh and used  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst samples visualize above mentioned structural change (Fig. 2A,B). The fresh catalyst contains round-shape, probably partially amorphous  $\text{Ni}_2\text{P}$  particles, whereas the particles of the used catalyst look like crystals terminated by well-formed flat low energy facets. The average size of  $\text{Ni}_2\text{P}$  particles seems to be the same in both the activated and the used catalysts suggesting that mainly re-structuring of the  $\text{Ni}_2\text{P}$  particles occurred during the catalytic reaction and not much sintering. The carbonyl band at  $2090\text{ cm}^{-1}$  is the dominating band if the  $\text{Ni}_2\text{P}$  crystals on the TEM picture show flat terminating facets, suggesting that the band belongs to CO adsorbed on mentioned crystal faces. The broadening of the band at the low frequency side (a shoulder around  $2050\text{ cm}^{-1}$ ) is probably due to CO adsorption on the higher index crystal faces.

The CO spectrum of the activated  $\text{Ni}_2\text{P}/\text{SBA-15}$  catalyst shows much similarity to the CO spectrum of the used than to the activated  $\text{Ni}_2\text{P}/\text{SiO}_2$  (cf. Fig. 4A,a; 4B,a and 4C,a). The carbonyl band at  $2096\text{ cm}^{-1}$  is very strong, whereas the  $2195\text{ cm}^{-1}$  band of the  $\text{Ni}^{2+}$ -CO species is weak (Fig. 4C,a). Notice that the SBA-15 supported catalyst precursor was reduced at higher temperature than  $\text{SiO}_2$  supported preparation to generate  $\text{Ni}_2\text{P}$  phase. This may explain the found morphological differences of the activated catalysts.

### *Propylamine hydrodenitrogenation*

In Fig. 6, PA hydroconversion and selectivity is shown over silica supported Ni and  $\text{Ni}_2\text{P}$  catalysts as a function of the reaction temperature. The products of PA HDN are propane and ammonia. DPA and TPA appeared as by-products in concentration that depended on the

reaction conditions and the activity of the catalyst (Figs. 6A-C). The direct C-N bond hydrogenolysis of PA gives equivalent amount of ammonia and propane. However, no propane but ammonia is formed in the conversion of PA to DPA and TPA. In contrast, no ammonia but propane is formed by the C-N bond hydrogenolysis of DPA and TPA beside primary or secondary amine, respectively. One objective of the present study is to understand and describe the reaction network of the PA HDN reaction.

The reference catalyst Ni/SiO<sub>2</sub> was very active in the PA hydroconversion. About 80 % conversion was attained at temperature as low as 200 °C. The main reaction was the PA disproportionation to DPA and ammonia. Small amount of TPA was also formed (Fig. 6C,F). The virtual absence of propane in the product mixture at this low reaction temperature indicates that the catalyst is hardly active in the direct C-N hydrogenolysis of PA. Above about 300 °C reaction temperature ammonia, less propane, and significant amount of methane and ethane were obtained. This is not surprising because supported Ni catalysts are known about their high activity in C-C bond hydrogenolysis.

The silica supported Ni<sub>2</sub>P catalysts were less active in the PA conversion than the reference catalyst Ni/SiO<sub>2</sub>. The conversion, attained over the Ni catalyst already at 200 °C, was reached at 275 °C over Ni<sub>2</sub>P/SBA-15 and only at 350 °C over Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst (Fig. 6A,B,C). However, significant selectivity to propane and ammonia was observed already at low temperature, showing that the Ni<sub>2</sub>P catalysts are active in the C-N hydrogenolysis (Fig. 6D,E). At higher temperatures the PA disproportionation became the main reaction as shown by the high DPA and reduced propane selectivity (Fig. 6D,E). Above about 300 °C the C-N bond hydrogenolysis speeded up again. Propane and ammonia became the main products. It is to be noticed that nearly full HDN of PA could be attained using silica-supported Ni<sub>2</sub>P catalysts while C-C hydrogenolysis did not occur at all.

The effect of H<sub>2</sub> partial pressure on PA hydroconversion over Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is demonstrated by Fig. 7. The propane yield was hardly affected by the increased H<sub>2</sub> pressures at low temperatures. However, at temperatures where mainly the DPA and TPA products were further converted the higher H<sub>2</sub> pressures suppressed the conversion of DPA and, thereby the total PA conversion. As a result the DPA yield and selectivity stabilized at a higher level on expense of a lower propane yield and selectivity (Fig. 7).

### *In situ DRIFT spectroscopy*

Difference infrared spectra of species, obtained by subtracting the spectrum of the catalyst from the more complex spectrum of the catalyst and the reacting PA/H<sub>2</sub> mixture are presented in Figs. 8 and 9. Because the spectral features and their responses to changed reaction conditions were very similar for catalysts Ni<sub>2</sub>P/SiO<sub>2</sub> and Ni<sub>2</sub>P/SBA-15, the results obtained for the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst is discussed here in more details.

Involvement of hydroxyl groups in H-bonding interaction generally induces bathochromic shift of the  $\nu_{\text{OH}}$  frequency. In the difference spectrum the shift generate negative band at the original position of the  $\nu(\text{OH})$  band and broad more intense positive band(s) at lower wavenumbers. The appearance of negative  $\nu_{\text{OH}}$  bands in the difference spectrum indicates that surface hydroxyl groups of the catalyst are consumed or perturbed by adsorption interaction with reactant or product molecules. The appearance of positive bands unequivocally shows formation of a new species. Negative bands in the  $\nu(\text{OH})$  region appeared at 3740, 3665, and  $\sim 3520\text{ cm}^{-1}$ . The band at  $3740\text{ cm}^{-1}$  and the broad band at about  $3520\text{ cm}^{-1}$  (not labeled on the spectra) are assigned to free and associated silanol groups, respectively, suggesting that molecules from the reacting mixture interact with the Si-OH groups via hydrogen bonding. H-bonding with the strong nitrogen bases generates strong broad  $\nu_{\text{OH}}$  bands shifted to the  $3200\text{-}2700\text{ cm}^{-1}$  wavenumber region where they can not be resolved due to overlapping with each other and other bands (vide infra).

The hydroxyl groups, linked to phosphorous, give band at  $3665\text{ cm}^{-1}$ . The appearance of a negative band at  $3665\text{ cm}^{-1}$  was found to be paralleled by the appearance of positive bands stemming from protonated nitrogen bases (vide infra). These finding suggests that, in contrast to silanol groups, the P-OH groups are acidic enough to donate protons to the strong nitrogen bases, present in the reacting gas (Fig. 8A, a).

The strong overlapping absorption bands around  $3000\text{ cm}^{-1}$  can be attributed to asymmetric and symmetric  $\nu(\text{CH}_3)$  and  $\nu(\text{CH}_2)$  stretching vibrations of methyl and methylene groups of the adsorbed species. The corresponding deformation vibrations of the groups appear at  $1460\text{ cm}^{-1}$  ( $\delta_{\text{as}}(\text{CH}_3)$ ,  $\delta(\text{CH}_2)$ ) and  $1400\text{ cm}^{-1}$  ( $\delta_{\text{s}}(\text{CH}_3)$ ,  $\omega(\text{CH}_2)$ ) [27-29].

The assignment of the bands of gaseous, adsorbed, and protonated N-bases, obtained from the HDN reaction is given in Table 2. Similar absorption bands at 3360, 3290, and  $3160\text{ cm}^{-1}$  were observed before from the adsorption of ethylamine over WP/SiO<sub>2</sub> and assigned to protonated amine  $\text{C}_2\text{H}_5\text{NH}_3^+$  [30]. However, from the adsorption of PA on surfaces not carrying Brønsted acid sites, such as silica or sodium zeolites, virtually the same absorption bands were obtained [29,31]. Latter results clearly show that these bands can not belong to

protonated alkylamines. The bands at 3360 and 3290  $\text{cm}^{-1}$  can be assigned to the  $\nu_{\text{as}}(\text{NH}_2)$  and  $\nu_{\text{s}}(\text{NH}_2)$  vibrations of the amine group of adsorbed primary amine, whereas the band at about 3160  $\text{cm}^{-1}$  stems from the first overtone of the  $\beta_{\text{s}}(\text{NH}_2)$  vibration mode having the frequency of 1595  $\text{cm}^{-1}$  (Fig. 8B, a) [27,29]. Additional bands are discernible at about 1620  $\text{cm}^{-1}$  on the high frequency side of the 1595  $\text{cm}^{-1}$  band, and also a well separated band at 1530  $\text{cm}^{-1}$ . The species obtained from adsorption of alkylamine over solid Brønsted acids gave similar bands, which were assigned as the  $\delta_{\text{as}}(\text{NH}_3^+)$  and  $\delta_{\text{s}}(\text{NH}_3^+)$  vibrations of the protonated amine [31-33]. The  $\delta_{\text{s}}(\text{NH}_3^+)$  band at 1530  $\text{cm}^{-1}$ , not overlapping with any other band, is particularly useful to follow the conversion of alkylamines to surface bound alkylammonium species. The  $\nu(\text{NH}_3^+)$  band should appear as a strong broad band between 3200-2700  $\text{cm}^{-1}$  [27,28]. The strong  $\nu(\text{OH})$  bands of silanol groups, which are H-bonded to nitrogen bases are shifted in the very same spectral region [34], generating a broad envelope of overlapping bands.

The absorption band at ~1105  $\text{cm}^{-1}$  (Fig. 8B) can be assigned to the  $\nu(\text{C-N(H)})$  vibration of adsorbed PA [27,28]. When the reaction temperature was raised this band became weaker and new bands developed at about 2815 and 1140  $\text{cm}^{-1}$  (Fig. 8A and B, b-d), corresponding to vibration frequencies of symmetric  $\text{CH}_2(\text{N})$  and  $\text{C-N(C)}$  stretching vibrations, respectively [27,28]. Therefore, we attribute the appearance of these spectral features to DPA formed by PA disproportionation. The  $\delta(\text{NH})$  vibration of aliphatic secondary amines is generally very weak, thus its contribution to the band observed around 1600  $\text{cm}^{-1}$  must be negligible. Note that bands of DPA gain intensity as the reaction temperature is increased from 250 to 300 and 350 °C. However, at 400 °C the band becomes much weaker (Fig. 8A and insert). While dipropylamine disappears from the reaction system, bands of gas phase ammonia appear at 965-930 (inversion doubling), 1626 and 3334  $\text{cm}^{-1}$  with rotational side bands. These results substantiate that DPA is intermediate of the PA HDN reaction, which is in full agreement with the catalytic results (Fig. 6).

A low intensity doublet at 2530 and 2400  $\text{cm}^{-1}$  is also discernible in the spectra (Fig. 8A). Because similar bands were not obtained from adsorption of alkylamine over silica supports [29,31], it seems most probable that these bands stem from the  $\nu_{\text{as}}(\text{NH}_2^+)$  and  $\nu_{\text{s}}(\text{NH}_2^+)$  vibrations of protonated surface-bound DPA [27,28]. These bands, together with the  $\delta_{\text{s}}(\text{NH}_3^+)$  band of protonated PA ( $\text{PAH}^+$ ) at 1530  $\text{cm}^{-1}$  appear with lower intensity over the  $\text{Ni}_2\text{P/SBA-15}$  catalyst (Fig. 9). This was accounted for the lower concentration of the P-OH related strong Brønsted acid sites in the latter sample. Indeed, the P-OH band of the  $\text{Ni}_2\text{P/SBA-15}$  catalyst was weaker than that of the  $\text{Ni}_2\text{P/SiO}_2$  catalyst (not shown).

The changing band intensity shows that the surface concentration of  $\text{PAH}^+$  varies with the reaction temperature (Fig. 8). However, this surface concentration did not show any correlation with the concentration of the DPA. These results suggested that the  $\text{PAH}^+$  species are spectator species in the DPA-forming reaction. In order to further clarify the role of strong Brønsted acid sites in the PA disproportionation reaction, Ni/SiO<sub>2</sub> catalyst, not having strong acid P-OH sites, was also investigated.

Infrared spectra of surface species formed from PA/H<sub>2</sub> mixture over Ni/SiO<sub>2</sub> catalyst are shown in Fig. 10. Because this catalyst was more active than the Ni<sub>2</sub>P/silica catalyst (Fig. 6C) the first spectrum was recorded at temperature as low as 100 °C (Fig. 10, a). Virtually the same surface species were identified than over the silica-supported Ni<sub>2</sub>P catalyst (cf. Figs. 8 and 10, spectra a) but, in absence of strong Brønsted acidity, no bands of  $\text{PAH}^+$  appeared.

The bands of DPA and reaction product NH<sub>3</sub> appeared already at reaction temperature 200 °C (Fig. 10). Notice the bands at 2815 cm<sup>-1</sup> ( $\nu_s(\text{CH}_2(\text{N}))$ ) and 1140 cm<sup>-1</sup> ( $\nu(\text{C-N}(\text{C}))$ ) and the sharp bands of gas phase ammonia (Fig. 10, spectra b). At reaction temperatures 300 °C and above DPA started to become converted to gas phase hydrocarbon and ammonia (Fig. 10, b-d). At the highest reaction temperature (400 °C) the spectrum is dominated by the sharp vibration band of gas phase CH<sub>4</sub> at 3015 cm<sup>-1</sup> and its rotational side bands. These spectral changes are in full agreement with the catalytic results and suggest that the HDN reaction of PA follows a similar pathway on the supported Ni catalyst than over the Ni<sub>2</sub>P catalyst. However, the former catalyst shows high activity also in the hydrogenolysis of the C-C bonds leading to fragmentation of the hydrocarbon chain (cf. Figs. 10 and 6C).

## 4. Discussion

### *Catalyst topology*

The strength of the C≡O bond and, as a consequence, the  $\nu(\text{CO})$  frequency of surface carbonyl species strongly depends on the chemical environment and the electronic state of the adsorption site. Provided that the kinds of carbonyls can be assigned to specific surface formations conclusions can be drawn about the relative amounts of the different sorption sites. Together with TEM examinations the CO adsorption studies permit to draw conclusions about the topology of the catalyst surface.

The carbonyl band of the silica supported Ni<sub>2</sub>P at 2195 cm<sup>-1</sup> was assigned to weakly bound CO but the assignment of the species to specific adsorption sites remained a matter of

discussion. Layman et al. [21,24] attributed a similar band to  $\nu_{\text{CO}}$  vibration of a  $\text{P}=\text{C}=\text{O}$  species. In light of present results this assignment seems to be doubtful. Over the surface of the passivated  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst significant fraction of the surface Ni and P atoms are in an oxidation state of +2 and +5, respectively in Ni-phosphate-like species [8,9,10,21]. The band at  $2195\text{ cm}^{-1}$  is stronger in the spectrum of this catalyst than in that of the  $\text{H}_2$ -activated catalyst (vide infra). In line with the finding of Busca et al. [19] we found that the modified silica, containing surface phosphate and hydrogen phosphate groups does not adsorb CO (Fig. 4B, f). These results substantiate that the band at  $2195\text{ cm}^{-1}$  belongs to  $\text{Ni}^{2+}$ -CO species. This assignment is supported by earlier results of Hadjiivanov et al. [23].

Jensen et al. [25] shortly described the FT-IR spectra of CO adsorbed at room temperature on reduced  $\text{Ni}/\text{SiO}_2$  catalyst. At CO pressure near to that applied in the present study bands were obtained from adsorption at  $2067$  and  $1887\text{ cm}^{-1}$  assigned to terminal and bridging CO, respectively, bound to Ni metal particles. Moreover, bands appeared at  $2035$  and  $2002\text{ cm}^{-1}$ , stemming from CO bound to defect sites of Ni particles and to the support, respectively. The higher  $\nu(\text{CO})$  frequency of the carbonyls, linearly bound to silica-supported  $\text{Ni}_2\text{P}$  catalyst ( $2090$ - $2096\text{ cm}^{-1}$ , Fig. 4) compared to the corresponding frequency of the carbonyls bound to  $\text{Ni}/\text{silica}$  ( $2067\text{ cm}^{-1}$ ) catalyst was attributed to the electron withdrawing properties of the P atoms generating a minor positive charge on the Ni atoms ( $\text{Ni}^{\delta+}$ ) [21,24]. Nevertheless, the Ni-P bond is covalent and the  $\text{Ni}_2\text{P}$  phase exhibit metallic character [8,24,35]. Despite the metallic character of  $\text{Ni}_2\text{P}$  no bridging carbonyl was formed over the  $\text{Ni}_2\text{P}/\text{SiO}_2$ . It was argued that the larger distance of surface nickel atoms in  $\text{Ni}_2\text{P}$  does not allow the formation of such species [22]. Unlike the carbonyls of the  $\text{Ni}/\text{SiO}_2$  [25] the carbonyls of the  $\text{Ni}_2\text{P}/\text{SiO}_2$ , giving the bands at  $2096$  and  $2035\text{ cm}^{-1}$ , resist flushing by He flow even at temperatures as high as  $100\text{ }^\circ\text{C}$  (Fig. 4A, c). Due to stronger  $\pi^*$  back-bonding carbonyls over surfaces of higher electron density have lower  $\nu(\text{CO})$  frequency, weaker C-O bond, than over surfaces of lower electron density, whereas the carbonyl groups bind stronger to sites of higher electron density [22,26,36]. Thus, the carbon monoxide bound to higher-energy sites of nickel, such as steps, kinks, corners, and edges, shows stretching mode with lower frequency than that adsorbed on terrace atoms [26]. The band at  $2096$  and  $2035\text{ cm}^{-1}$  are assigned here to CO adsorbed on terrace atoms of crystal faces and on high-energy defect sites, respectively. The strong band at  $2035\text{ cm}^{-1}$  (Fig. 4A) suggests that the  $\text{Ni}_2\text{P}$  particles of the fresh catalyst contain defect sites in high concentration. The small particles have rather disordered structure. Some of them may contain even residual nickel phosphate. It has to be



noticed that adsorption on defect sites of Ni<sub>2</sub>P particles not only gives a  $\nu(\text{CO})$  band shifted to lower wavenumbers but also produces ideal conditions to dipolar coupling interactions between the nearby carbonyl species of slightly different vibration frequencies. As a consequence the lower frequency species transfers intensity from its band to that of the higher frequency counterpart. This intensity transfer strengthens the 2096 cm<sup>-1</sup> band of the terrace-bound CO promoting the detection of this species (Fig. 4A), however, makes the quantitative interpretation of the spectrum very difficult.

The carbonyl species giving band at 2035 cm<sup>-1</sup> could not be detected at all over the Ni<sub>2</sub>P catalysts, already used in HDN reaction (Fig. 4B,D). The absence of this band does not necessarily indicate the total absence of defect Ni<sub>2</sub>P sites. As was pointed out by Hollins [36], just a few percent increase in the proportion of the high-frequency species was enough that the band of this species should dominate the infrared spectrum due to effect of dipolar coupling. It is obvious that the Ni<sub>2</sub>P phase took up an ordered crystal form under reaction conditions (Fig. 2B). The particle size of the SiO<sub>2</sub> supported Ni<sub>2</sub>P phase remained about the same, but the morphology changed from about globular particles, carrying virtually defect sites only, to particles with flat faces (Fig. 2A,B).

It follows from the above discussion that the Ni<sub>2</sub>P/SBA-15 catalyst must contain less amorphous and defected Ni<sub>2</sub>P particles and phosphate residue than the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst (Fig. 4C). The CO species, having lower  $\nu(\text{CO})$  frequency, must be bound stronger than the species absorbing at higher frequency. The integrated intensity of both bands decreases when the CO coverage of the catalyst is decreased. In accordance with the strengths of adsorption the relative intensity loss of band at 2035 cm<sup>-1</sup> is smaller than that of the band at 2096 cm<sup>-1</sup> (Fig 4, A and C). When the coverage is further decreased the high-frequency band is expected to disappear first and the low frequency band after. Interestingly, after disappearance of the low-frequency band a band remained at 2080 cm<sup>-1</sup> (Fig. 4C). Similar  $\nu(\text{CO})$  band was obtained from the adsorption of CO over silica supported Ni catalysts [21,26]. The band at 2080 cm<sup>-1</sup> suggests that a small fraction of the Ni precursor was reduced to Ni<sup>0</sup> even in the presence of excess amount of P precursor on the SBA-15 silica surface.

Because the Ni<sub>2</sub>P particles were inside the narrow channels of the SBA-15 support, the pore size of the support somewhat limited the size and morphology change of the Ni<sub>2</sub>P particles (Fig. 2C and D). A salient finding of the CO chemisorption and TEM study of the present work is that the structure and the surface of the working catalyst are quite different than that of the H<sub>2</sub> activated one. Interestingly, neither the CO chemisorption capacity nor the

size of the Ni<sub>2</sub>P particles in the activated and the used catalyst differs as drastically as the morphology of the particles.

The assignment of the band at 2055 cm<sup>-1</sup> also raises questions (Fig. 4 A,a; C,a). Both the silica supported Ni<sub>2</sub>P and Ni catalysts were found to bind CO as species giving such infrared band. It was assigned first to volatile Ni(CO)<sub>4</sub> formed from CO and supported Ni and adsorbed on the support [23,24]. However, we do not believe that the similar band obtained from CO adsorption over Ni<sub>2</sub>P/SiO<sub>2</sub> stems from adsorbed Ni(CO)<sub>4</sub>. The formation of Ni(CO)<sub>4</sub> over Ni<sub>2</sub>P must be strongly hindered [24]. The band at ~2055 cm<sup>-1</sup> disappeared when the CO gas was flushed out from the DRIFTS cell by He flow. This event was paralleled by the strengthening of the bands at 2096 and 2035 cm<sup>-1</sup> (Fig. 4A,a,b and C,a,b). Therefore we attribute the ~2055 cm<sup>-1</sup> band to nickel subcarbonyl species Ni(CO)<sub>x</sub> (x<4) that is transformed to monocarbonyl when the CO coverage of the surface is decreased.

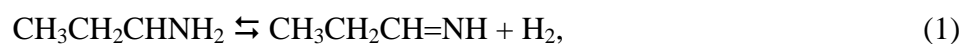
Because it is important that the organic N-compound, such as the alkyl amine should bind near to the site where the H<sub>2</sub> is activated it was argued that at least a fraction of the P-OH groups must belong to the active hydrogenation phase to promote the interaction of the hydrogen and the nitrogen base [22,37]. It was suggested that the hydroxyl groups would come from phosphate species of the passivated catalyst that did not become fully reduced in the activation treatment by H<sub>2</sub>. However, only a single kind of the P-OH group was detected on the surface of the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst by DRIFT spectroscopy (Fig. 5). The ν(OH(P)) band was virtually the same strength regardless of the presence or absence of passivating phosphate-like surface layer on the Ni<sub>2</sub>P particles. These results suggested that most of the P-OH groups come from silica-bound hydrogen phosphate and only a very small fraction of the surface P-OH groups may belong to the nickel-containing active phase. The carbonyl band at 2195 cm<sup>-1</sup> (Fig. 4A), assigned to Ni<sup>2+</sup>-CO, substantiates the presence of residual Ni<sup>2+</sup> in the activated catalyst, however, we do not have information about the location of these nickel ions and evidence about the presence of P-OH near to the surface of Ni<sub>2</sub>P particles.

Two kinds of Ni atoms are distinguished in the Ni<sub>2</sub>P crystals regarding the number of the nearest coordinating P atoms, namely, four and five coordinated Ni atoms, designated as Ni(1) and Ni(2), respectively [38]. Both kinds of Ni atoms are present on the surface of the Ni<sub>2</sub>P crystals but Ni(2) was shown to be the dominating surface Ni atom in the catalysts containing highly dispersed Ni<sub>2</sub>P particles [38]. The present work clearly shows that the Ni<sub>2</sub>P particles have a highly defected structure in their initial reduced state of the catalyst. This structure substantiates that the surface of the particles is covered predominantly by Ni atoms

in low coordination. This structure, having high electron density nickel atoms, were quite stable in hydrogen at the temperature of the reaction, but was rapidly converted to ordered crystals in contact with the PA reactant. It is rather common that adsorption interaction at elevated temperature increases the mobility of the atoms on a solid surface and promotes reorganization of the surface structure. In other words the catalytically active surface ensembles are generated in the interaction of the reactant and the catalyst. This finding points out the significance of operando methods in catalysis research.

### *PA hydroconversion*

The results shown in Fig. 6 suggest that at lower reaction temperatures propane and ammonia, as well as, DPA and ammonia are predominantly primary products, obtained from PA by C-N bond hydrogenolysis and PA disproportionation, respectively. As the temperature was increased the DPA yield decreased while the propane yield increased at unchanged conversion. These results suggest that at higher temperatures the propane is formed mainly in consecutive reaction through hydrogenolysis of DPA intermediate. The PA disproportionation was studied by Geus et al. [39] over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at 5.6 kPa PA partial pressure and different H<sub>2</sub> partial pressures below 1 bar at 150 °C. In absence of hydrogen the catalyst was found to rapidly lose activity. In the presence of hydrogen DPA and ammonia were the only products. In line with the findings of Geus et al. [39] we found that increased hydrogen pressure suppressed the conversion of PA to DPA. This indicates that reaction of alkylamine HDN has complex chemistry. The effect of increased hydrogen pressure infers that disproportionation goes through an unsaturated intermediate, most probably through 1-propaneimine [39]. Thus, the dimerization can be described in steps of (i) PA dehydrogenation, (ii) acid catalyzed addition of PA to the obtained 1-propaneimine, (iii) the deamination of the thus obtained 2-amino dipropylamine to get the Schiff base propylidene propylamine, and finally (iv) the hydrogenation of the Schiff base to DPA. This outline of the process assumes that the catalyst is bifunctional, having both hydrogenation-dehydrogenation and Brønsted acid sites. This picture provides explanation for the finding that increased H<sub>2</sub> pressure suppressed the DPA formation over Ni<sub>2</sub>P/silica catalysts by suppressing the dehydrogenation reaction



which reaction is the first step towards PA dimerization. This reaction also explains the temperature effect on the activity. At relatively low temperature the catalyst is able to activate hydrogen to break the C-N bond, however, the DPA formation and the conversion of PA remains low. Higher reaction temperatures shift the hydrogenation-dehydrogenation equilibrium in the direction of dehydrogenation. For instance, if the temperature is changed from 200 to 400 °C the equilibrium constant of Eq. (1) increases from  $9 \times 10^{-10}$  to  $2 \times 10^{-7}$ . In acid catalyzed reaction with PA the 1-propaneimine intermediate is rapidly consumed promoting further PA dehydrogenation and DPA formation. At about 275-350 °C the PA conversion reaches its maximum. The main product and the main surface species becomes the DPA. At higher temperatures again the hydrogenolysis of DPA and PA C-N bonds becomes the prevailing reaction, giving propane and ammonia.

It is important to note that no full conversion of PA could be reached on the Ni<sub>2</sub>P catalysts (Figs. 6A,B), which might indicate equilibrium limitation. Reaction of propane with ammonia to form propylamine under applied conditions is very unlikely. However, in the presence of catalyst the addition of ammonia to propene is a facile reaction. The reaction is catalyzed either by acidic [40], basic [41] and metallic [42] active sites. The studied Ni<sub>2</sub>P/silica catalytic system has both metallic hydrogenation/dehydrogenation activity and acidic properties. The propane must be in equilibrium with propene. This equilibrium favors propene especially at the high H<sub>2</sub> pressure and at the relatively low temperature of the HDN reaction. Nevertheless, the facile catalytic ammonia addition to olefin can establish a propane/propene/propylamine/ammonia equilibrium, where the propene concentration remains extremely low, but full propylamine conversion cannot be achieved, unless the catalyst is active in the HDN reaction but inactive in the reaction of ammonia addition to olefin.

The hydrogenolysis of the C-N bonds of PA results in propane and ammonia as primary products. The conversion of PA to DPA and TPA gives ammonia also as primary product and no propane. The propane obtained from the C-N hydrogenolysis of primary product DPA or TPA is secondary product. Thus, ammonia must be always primary product, whereas results suggest that propane can be formed both ways. It is primary product at low temperatures and secondary product at high temperatures. The analysis of conversion curves obtained at lower and higher temperature (Fig. 11A,B) was applied to support this statement. Extrapolation of selectivities to zero conversion, sometimes referred to as first-rank Delplot analysis [43,44], helps to distinguish primary and secondary products of complex reaction networks. Plot with

non-zero intercept shows that the corresponding species is primary product. In accordance with above discussion the plots for ammonia (Fig. 11C,D) show that ammonia is primary product regardless of the reaction temperature. The Delplots of DPA also satisfy the criterion expected from a first rank product (Fig. 11C,D). In contrast, when the reaction temperature is increased, the intercept from propane changes as expected from finite to near zero indicating the rank alteration of the propane product.

No DPA was formed from PA over silica support but it was formed over both the Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts. Neither the active phase nor the support of Ni/SiO<sub>2</sub> and Ni<sub>2</sub>P/SiO<sub>2</sub> are the same. The Ni is distributed over a silica support, not having acid sites that were able to protonate even the strong base PA, whereas the Ni<sub>2</sub>P is distributed over silica surface, carrying Brønsted acid P-OH groups, which were able to protonate N-bases. The active phases show hydrogenation/dehydrogenation activity and DPA is formed over both catalysts. The need for hydrogenation/dehydrogenation activity substantiates that DPA is formed through intermediate obtained by PA dehydrogenation, most probably through propaneimine. However, bands of propaneimine and protonated propaneimine could not be resolved from the complex operando DRIFT spectra, whereas the bands of DPA appeared. The surface concentration of the reaction intermediate propaneimine must be very low, because the equilibrium of Eq. (1) is shifted to the left at high H<sub>2</sub> pressure. The imine concentration is further decreased by its rapid conversion to DPA. Researchers often approach the problem of detecting intermediate by applying reaction conditions, which favor the formation of the intermediate and does not favor its conversion. It was possible to detect vibration bands of C=N- group at 1670 cm<sup>-1</sup>, if we contacted the Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst with PA/He flow under reaction conditions. The corresponding DRIFTS spectra are shown in Fig. S3. It was claimed by Geus et al. [39] that beside dehydrogenation function Brønsted acid function is also needed to induce the addition of PA to 1-propaneimine. Interestingly DPA was generated also over non acidic Ni/SiO<sub>2</sub> catalyst. Results substantiate that Brønsted acid active sites are not necessary for the PA disproportionation and, therefore, probably play negligible role in the PA hydroconversion.

## 5. Conclusions

It is possible to obtain high yields of hydrocarbon and ammonia product from N-containing organic compounds, such as pyro-oil from animal by-products by catalytic HDN. The silica-supported nickel phosphide is active catalyst of the process. The reaction proceeds through secondary and tertiary amine intermediates. The results obtained with the model reactant

propylamine suggest that formation of dipropylamine by-product can be suppressed and high conversion can be achieved at 350-400 °C reaction temperature and moderate ( $\leq 30$  bar) H<sub>2</sub> partial pressures.

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**Table 1.** Characterization of catalysts.

Catalysts	SSA, <sup>a</sup> m <sup>2</sup> g <sup>-1</sup>	Ni, wt%	P, wt%	Dispersion, <sup>b</sup> %	D, <sup>c</sup> nm	D, <sup>d</sup> nm
Ni <sub>2</sub> P/SiO <sub>2</sub>	268 (563)	5.04	4.11	15.4 (41.4)	20-60	49 (55)
Ni <sub>2</sub> P/SBA-15	162 (800)	7.32	4.07	34.8 (114.2)	5-15	10 (10)
Ni/SiO <sub>2</sub>	558 (563)	6.76	-	9.2 (28.8)	2-10	11

<sup>a</sup> SSA= specific surface area, determined by the Brunauer-Emmett-Teller (BET) method (specific surface area of the support is given in parentheses).

<sup>b</sup> Dispersion of particles determined from H<sub>2</sub>-TPD measurements. The amount of H<sub>2</sub> evolved (μmol H<sub>2</sub>/g<sub>cat</sub>) is given in parenthesis. <sup>c</sup> Diameter of particles of the active phase observed in the TEM micrograph. <sup>d</sup> particle size calculated from XRD by Scherrer equation (particle size for used catalyst is given in parentheses).

**Table 2.** Bands obtained from the HDN reaction of PA over silica-supported Ni<sub>2</sub>P and Ni catalysts. <sup>a</sup>

Species	Frequency, cm <sup>-1</sup> (Vibrational mode)
Propylamine (PA)	3360 (ν <sub>as</sub> (NH <sub>2</sub> )), 3290 ((ν <sub>s</sub> (NH <sub>2</sub> )), 3160 (2×β <sub>s</sub> (NH <sub>2</sub> )) <sup>b</sup> , 1595 (β <sub>s</sub> (NH <sub>2</sub> )), <b>1105 ν(C-N(H))</b>
Propylammonium ion (PAH <sup>+</sup> )	3200-2700(ν(NH <sub>3</sub> <sup>+</sup> )) <sup>c</sup> , 1620(δ <sub>as</sub> (NH <sub>3</sub> <sup>+</sup> )), <b>1530 (δ<sub>s</sub>(NH<sub>3</sub><sup>+</sup>))</b>
Dipropylamine (DPA)	<b>2815 (ν<sub>s</sub>(CH<sub>2</sub>(N))), 1140 ν(C-N(C))</b> , 1600 δ(NH) <sup>d</sup>
Dipropylammonium ion (DPAH <sup>+</sup> )	<b>2530 (ν<sub>as</sub>(NH<sub>2</sub><sup>+</sup>)), 2400 (ν<sub>s</sub>(NH<sub>2</sub><sup>+</sup>))</b>
Ammonia (NH <sub>3</sub> )	<b>3334 (ν<sub>s</sub>(NH)), 1626 (δ<sub>as</sub>(NH)), 965- 930 (δ<sub>s</sub>(NH))</b>
Ammonium ion (NH <sub>4</sub> <sup>+</sup> )	3200-2900 (ν(NH <sub>4</sub> <sup>+</sup> )) <sup>b</sup> , 1500-1400 (δ(NH <sub>4</sub> <sup>+</sup> )) <sup>e</sup>

<sup>a</sup> The bands given in bold are considered diagnostic regarding the catalytic PA HDN mechanism. <sup>b</sup> First overtone of β<sub>s</sub>(NH<sub>2</sub>) at 1595 cm<sup>-1</sup>. <sup>c</sup> Strong broad band overlapping with red shifted ν<sub>OH</sub> bands. <sup>d</sup> Very weak band hardly discernable due to overlapping with the strong (δ<sub>as</sub>(NH<sub>2</sub>)) band. <sup>e</sup> Broad band overlapping with CH deformation bands.

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## Figure captions

**Fig. 1.** (A) H<sub>2</sub>-TPR curves measured over the catalyst precursors of Ni/SiO<sub>2</sub>, Ni<sub>2</sub>P/SBA-15, and Ni<sub>2</sub>P/SiO<sub>2</sub> catalysts, and (B) XRD patterns of the corresponding catalyst samples reduced in H<sub>2</sub> at the indicated temperature for 3 h.

**Fig. 2.** TEM micrographs of fresh and used (A,B) Ni<sub>2</sub>P/SiO<sub>2</sub> and (C,D) Ni<sub>2</sub>P/SBA-15 catalysts.

**Fig. 3.** DRIFT spectra of the (A)  $\nu_{OH}$  region of the (a) fresh and (a1) used Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst. Spectra b and b1 are the corresponding spectra of the Ni<sub>2</sub>P/SBA-15 catalyst. Before spectra were recorded at room temperature the samples were pretreated *in situ* in the DRIFTS cell in H<sub>2</sub> flow at 550 °C for 1 h then was purged with He at 550 °C for 1 h. Section B shows the difference of the spectra of fresh and used (a) Ni<sub>2</sub>P/SiO<sub>2</sub> and (b) Ni<sub>2</sub>P/SBA-15 catalyst.

**Fig. 4.** DRIFT spectra of adsorbed CO on (A,B) Ni<sub>2</sub>P/SiO<sub>2</sub> and (C,D) Ni<sub>2</sub>P/SBA-15 catalysts. Spectra were taken either on the fresh (A,C) or used (B,D) catalyst samples at room temperature in the presence of gas phase CO in the IR cell (spectra a, a1 and f) and after purging the DRIFTS cell with He at room temperature (spectra b), 100 °C (spectra c), 200 °C (spectra d), and 300 °C (spectra e) for 10 min at each temperature. Spectrum (a1) was measured over the passivated Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst, whereas spectrum (f) was collected on the phosphated silica (PO<sub>x</sub>/SiO<sub>2</sub>) reference sample. Before spectra were recorded at room temperature the samples were pretreated *in situ* in the DRIFTS cell in H<sub>2</sub> flow at 550 °C for 1 h then was purged with He at 550 °C for 1 h.

**Fig. 5.** DRIFT spectra of the  $\nu_{OH}$  region of (a) phosphated silica (PO<sub>x</sub>/SiO<sub>2</sub>) sample, and (b) passivated Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst (dotted curve) after *in situ* treatment in He flow at 550 °C, and (c) Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst, after activation *in situ* in the DRIFTS cell in H<sub>2</sub> flow at 550 °C.

**Fig. 6.** Yields and selectivities of PA hydroconversion over (A,D) Ni<sub>2</sub>P/SiO<sub>2</sub>, (B,F) Ni<sub>2</sub>P/SBA-15, and (C,F) Ni/SiO<sub>2</sub> catalysts as a function of reaction temperature. Conversion of PA (■) and yield and selectivity values for the ammonia (○), propane (△), DPA (▽), TPA (◇), and

C1-C2 hydrocarbon (\*) products were measured at H<sub>2</sub> partial pressure of 27.3 bar, PA partial pressure of 2.7 bar and at WHSV of 1 g<sub>PA</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.

**Fig. 7.** Yields and selectivities of PA hydroconversion at H<sub>2</sub> partial pressures of 27.3 bar (full symbols), 40.5 bar (half-filled symbols), and 64.3 bar (empty symbols) as function of reaction temperature. The PA partial pressure and WHSV were 2.7 bar and 1 g<sub>PA</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, respectively.

**Fig. 8.** Difference DRIFT spectra obtained from the reaction of PA/H<sub>2</sub> over Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst at (a) 250 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C. Hydrogen was passed through a PA-containing saturator, kept at 0 °C, at a flow rate of 30 cm<sup>3</sup> min<sup>-1</sup>. The partial pressure of PA and the total pressure were 0.14 bar and 20 bar, respectively. Each spectrum was obtained by subtracting the spectrum of the catalyst in H<sub>2</sub> from the corresponding spectrum of the catalyst and the reacting gas.

**Fig. 9.** Difference DRIFT spectra obtained from the reaction of PA/H<sub>2</sub> over Ni<sub>2</sub>P/SBA-15 catalyst at (a) 250 °C, (b) 300 °C, (c) 350 °C, and (d) 400 °C. For further experimental conditions see the legend of Fig. 8.

**Fig. 10.** Difference DRIFT spectra obtained from the reaction of PA/H<sub>2</sub> over Ni/SiO<sub>2</sub> catalyst at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. For further experimental conditions see the legend of Fig. 8.

**Fig. 11.** Hydroconversion of PA (■) and yields of ammonia (○), propane (△), DPA (▽) and TPA (◇) as a function of the space time, and first rank Delplots of the products at 300 (A, C) and 375 °C (B, D). The PA and H<sub>2</sub> partial pressures were 2.7 and 27.3 bar, respectively.

## Figures

Fig. 1.

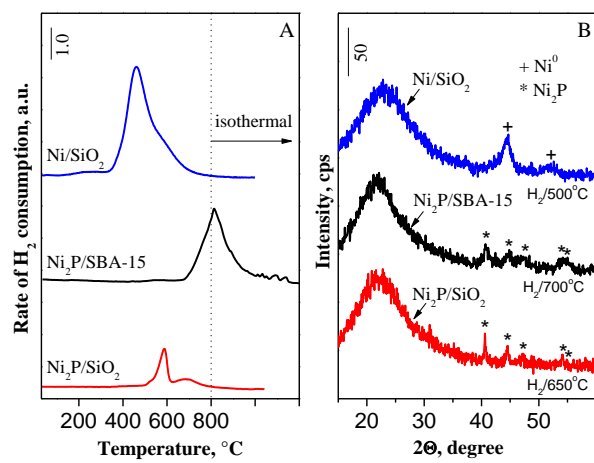


Fig. 2.

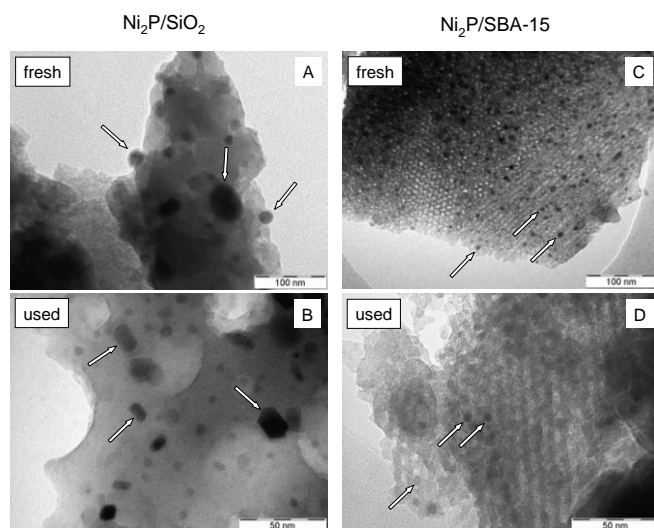


Fig. 3.

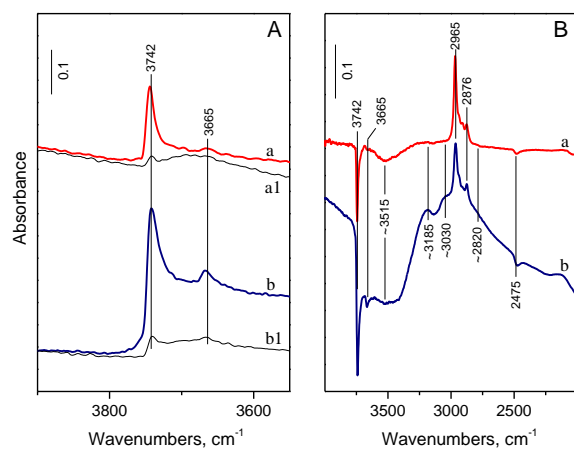


Fig. 4.

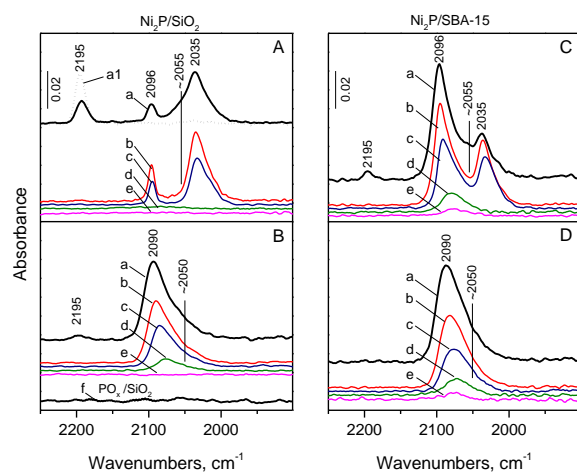


Fig. 5.

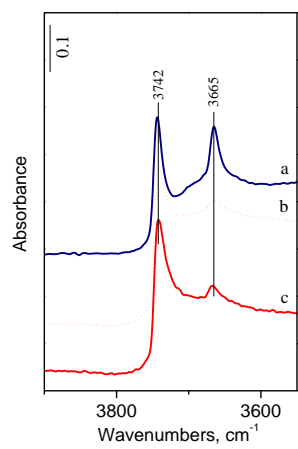


Fig. 6.

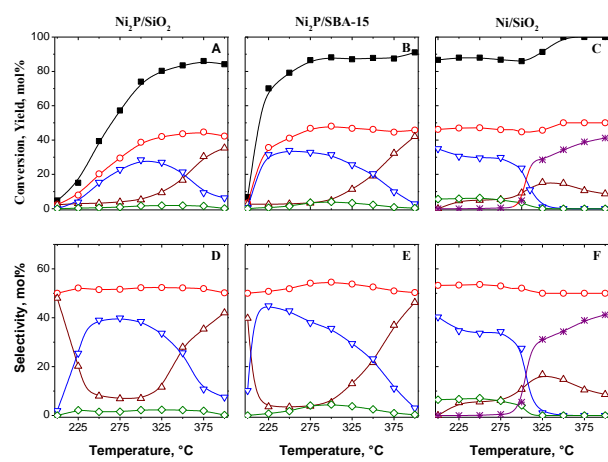


Fig. 7.

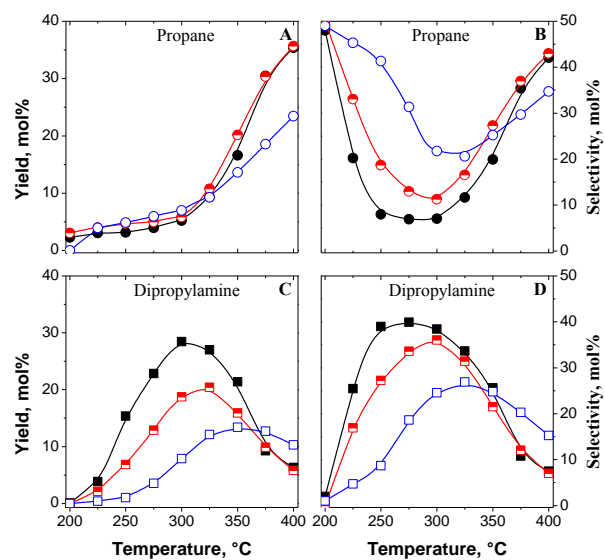


Fig. 8.

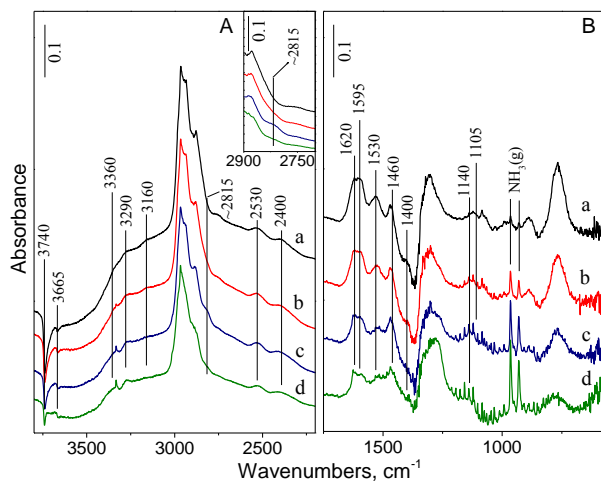


Fig. 9.

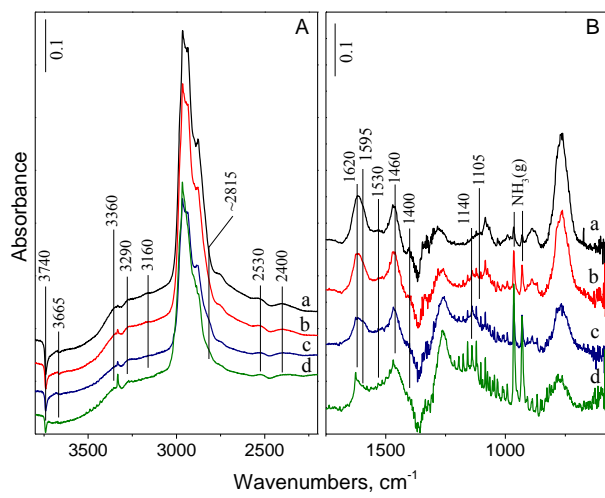


Fig. 10.

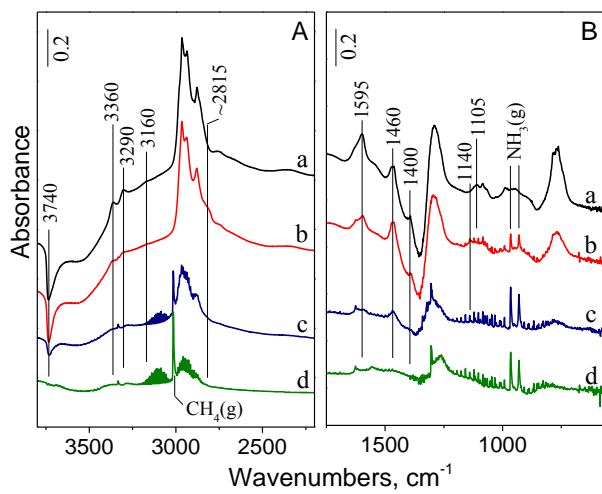




Fig. 11.

